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Thermodynamic and Structural Properties of Ethylene Copolymers

R. G. Alamo and L. Mandelkern*

Department of Chemistry and Institute of Molecular Biophysics, Florida State University, Tallahassee, Florida 32306. *Received June 23, 1988;
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ABSTRACT: The melting temperatures and degrees of crystallinity have been determined for a series of ethylene–1-alkene copolymers having both a most probable molecular weight distribution and a narrow composition distribution. These results are compared with those reported previously for a series of compositional fractions of the corresponding copolymers. These thermodynamic properties are found to be independent of the chemical nature of the counit. The importance of the sequence distribution of the counits in determining melting temperatures is again emphasized. The determinations of the level of crystallinity by different methods are compared and the differences that are observed attributed to specific aspects of the phase structure. The interfacial content is found to be independent of molecular weight.

Introduction

In an earlier study of the thermodynamic properties and phase structure of a variety of ethylene copolymers, we used dilatometry and calorimetry to measure the melting temperatures of well-characterized compositional fractions.[1] The melting temperatures obtained by dilatometry for a selected set of samples confirmed the results previously obtained by Richardson et al.[2] The melting temperatures were also determined by differential scanning calorimetry, after rapid crystallization from the melt, for the large number of copolymer fractions. These results showed that for copolymers that contain less than about 3 mol % branches, the ethyl-branched hydrogenated polybutadienes, the (diazoalkane) propyl-branched copolymers, the hexyl-branched copolymers, and the ethylene–vinyl acetate copolymers all follow the same melting temperature–composition relation. This relation is quite different for copolymers containing methyl[2,3] or chlorine side groups.[4] The melting temperatures for these copolymers are always greater at comparable counit contents. The hydrogenated polybutadienes, the ethylene–vinyl acetate copolymers, and those prepared by the decomposition of the diazoalkanes were shown to be in random sequence distribution. Since the long as well as bulky side groups cannot enter the crystal lattice, it was concluded that because of the identical melting temperature–composition relations branches of ethyl and larger were excluded from the crystalline phase. This conclusion was subsequently confirmed by solid-state carbon-13 NMR experiments by Laupretre et al.[5] and Perez et al.[6] The latter investigators concluded, based on a two-phase analysis, that the ratio of ethyl branches partitioned between the noncrystalline and crystalline phases was 10 to 1.

An important feature of the earlier work[1] was the significant differences in melting temperature that were observed between the composition fractions of the ethylene–1-butene copolymer that was studied and those of the other copolymers (see Figure 3 of ref 1). Since the hydrogenated polybutadienes were included in the latter grouping of copolymers, we observed differences in melting temperature for two copolymers having the same chemical-type branch group. The melting point differences ranged from 5 to 10 °C as the mole fraction of branch points increased from 0.5 to 3 mol %.

Continuing this earlier work, we have been able to study a series of ethylene–1-alkene random-type copolymers which were synthesized in such a way as to have a most probable molecular weight distribution as well as a narrow composition distribution. These characteristics avoid the need for fractionation and allow for more material to be available for study. We report the results here of the thermodynamic properties of these sets of copolymers and compare the results with those obtained previously.[1] Of particular interest is the influence of the mole fraction of branch points and the chemical nature of the side group on the melting temperature and on the level of crystallinity that is determined by different methods and the interfacial content.

Experimental Section

The ethylene copolymers studied in this work were prepared following the method of Kaminsky et al.[7] using $(C_5H_5)_2ZrCl_2$ as catalyst. (We thank the Polymers Group of the Exxon Chemical Company, Baytown, TX, for supplying us with these samples.) The three copolymers that were studied, ethylene–1-butene, ethylene–1-hexene, and ethylene–1-octene were studied as received.

The molecular characteristics of the copolymers are given in Table I. The weight- and number-average molecular weights were obtained by gel permeation chromatography following conventional procedures. It is clear that these samples follow a most probable molecular weight distribution. The determination of the counit content was carried out by carbon-13 NMR using the assignments reported in the literature.[8,9]

Melting temperatures were determined with a Perkin-Elmer DSC-2B calorimeter operating at a heating rate of 20 deg/min. The copolymers were rapidly crystallized in the DSC by bringing the temperature from the melt (150 °C) to −35 °C at the maximum rate possible by the instrument. Melting points were identified with the maximum in the endothermic peak. About 3 mg of sample was used in these experiments. From the DSC thermograms, the enthalpies of fusion were converted to degrees of crystallinity, $(1 - \lambda)_{\Delta H}$, by taking the enthalpy of a perfect polyethylene crystal to be 69 cal/g.[10]

The densities were obtained with samples initially quenched from the melt to −78 °C and then determined at 23 °C in a triethylene glycol/water density gradient calibrated with standard glass floats. The densities were converted to degree of crystallinity, $(1 - \lambda)_d$, by the specific volume relationship given by Chiang and Flory.[11] The Raman spectra in the internal mode region were obtained by using instrumentation that has been previously described.[12,13] The method of analysis to obtain α_c, the level of crystallinity; α_a, the liquid-like fraction; and α_b, the interfacial content, has also been detailed[12-14] following the initial work of Strobl and Hagedorn.[15]

We have deliberately adopted a rapid crystallization procedure (quenched) in the present work to enable a rational comparison to be made between the different specimens. After isothermal crystallization, or even slow cooling from the melt, the resulting melting temperatures and levels of crystallinity of random copolymers are very dependent on the details of the cooling process.[16] Even at a constant cooling rate, the counit concentration plays a crucial role in determining the sequences that actually crystallize

Table I
Molecular Characteristics of Ethylene Copolymers

copolymer	side group, mol %	M_w	M_w/M_n	T_m, °C	$(1 - \lambda)_{\Delta H}$	$(1 - \lambda)_d$	α_a	α_b	α_c
ethylene–butene	1.18	106 000	$\simeq 2$	109	0.36	0.47	0.51	0.09	0.36
ethylene–butene	1.91	99 000	$\cong 2$	103.5	0.32	0.46	0.60	0.12	0.28
ethylene–butene	1.90		$\cong 2$	100.3	0.30		0.66	0.09	0.25
ethylene–hexene	1.18	125 000	$\cong 2$	115	0.40	0.46	0.55	0.07	0.38
ethylene–hexene	1.21	48 800	1.87	114	0.40	0.52	0.51	0.11	0.38
ethylene–hexene	1.21	104 500	2.39	111.5	0.40	0.42	0.58	0.10	0.32
ethylene–hexene	1.43	18 875	2.39	113	0.51	0.58	0.43	0.11	0.46
ethylene–hexene	1.47	239 830	2.17	108.3	0.31	0.42	0.61	0.10	0.29
ethylene–hexene	1.48	112 000	$\cong 2$	108.8	0.36	0.43	0.59	0.09	0.32
ethylene–hexene	1.74	6 500	2.85	112	0.50		0.40	0.11	0.49
ethylene–hexene	1.74	80 000	$\cong 2$	100.1	0.31	0.40	0.64	0.10	0.26
ethylene–hexene	2.64	88 000	1.99	96.4	0.28	0.37	0.68	0.12	0.20
ethylene–hexene	3.52	40 000	2.00	85.6	0.19	0.31	0.67	0.18	0.15
ethylene–octene	2.14	83 00	$\cong 2$	99.7	0.28		0.62	0.18	0.20

and consequently the overall properties. Therefore, it is difficult following an isothermal or pseudoisothermal crystallization procedure to make a meaningful comparison between samples.

Results and Discussion

Melting Temperatures. The pertinent thermodynamic quantities concerned with the crystallization behavior of the copolymers are also given in Table I for the rapidly crystallized samples. In examining the extensive set of data for the ethylene-1-hexene copolymers, we find that for an approximately constant counit content the melting temperature decreases with increasing molecular weight. For example, for 1.74 mol % branch points, there is a 12-deg melting point decrease between molecular weights 6.5×10^3 and 8×10^4. For 1.4 mol % branch points, the difference is 5 deg between 1.9×10^4 and 2.4×10^5, while the difference is 3 deg for 1.2 mol % between 4.9×10^4 and 1.05×10^5. A similar effect has been noted previously with the hydrogenated polybutadienes.[17] This result is contrary to expectations for long-chain molecules.[18,19] We shall discuss the significance of these melting points in a subsequent report.[20] In addition to these ethylene-1-hexene data, an analysis of the melting temperatures of a very wide range of hydrogenated polybutadiene molecular weights will be given. In the present context, we limit ourselves to the major concern of comparing the melting temperatures of copolymers with different type side groups at comparable molecular weights. Consequently, in Figure 1 we have plotted the melting temperatures of the copolymers studied here in the molecular weight range 40–100 000. For comparative and reference purposes, two reference curves, obtained from Figure 3 of ref 1, are given. The dashed curve represents the results for the compositional ethylene-1-butene fractions that were studied previously. Their melting temperatures are indicated by the open squares. The solid curve represents the previous results for hydrogenated polybutadiene, ethylene-vinyl acetate, and ethylene-1-octene copolymers and copolymers having propyl side groups prepared by the decomposition of the appropriate diazoalkanes. The data points that fall of this curve represent the results from the present work. A significance feature of these results is that the melting temperatures of the new ethylene–butene, ethylene–hexene, and ethylene–octene are coincident with the previous data. The results are clearly independent of the chemical nature of the side group. Side groups as small as ethyl or as large as acetate and hexane display identical melting temperature–composition relations.

The fact that the melting temperatures of the new ethylene–butene copolymers fall on the same curve as the hydrogenated polybutadienes indicates that they possess a random sequence distribution. Previously, we found a substantially higher melting temperature for a different set of compositional fractions of ethylene–butene copolymers compared to the hydrogenated polybutadienes. This latter result was attributed to small differences in the sequence distribution parameter, p, in the well-known relation[21,22]

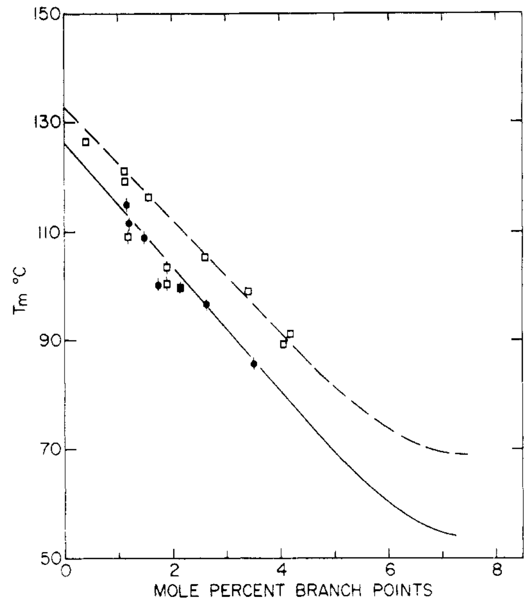

Figure 1. Plot of melting temperature against mole percent branch points for ethylene copolymers. Dashed and solid curves are reproduced from ref 1. (□) Compositional ethylene–butene fractions from ref 1. Copolymers with most probable molecular weight distribution: (□) ethylene–butene; (◆) ethylene–hexene; (◧) ethylene–octene.

$$\frac{1}{T_m} - \frac{1}{T_m{}^\circ} = -\frac{R}{\Delta H_u} \ln p \qquad (1)$$

Here T_m is the melting temperature characterized by p, $T_m{}^\circ$ is the melting temperature of the corresponding homopolymer, and ΔH_u is the enthalpy of fusion per repeating unit. It has been pointed out that for random type copolymers, in the composition range of interest, small variations in p can result in significant changes in the corresponding melting temperature. (Although eq 1 is derived for the equilibrium condition, the functional form is obeyed in nonequilibrium situations.)

Recently, Clas et al.[23] reported the melting temperature–compositions relations for a set of ethylene–butene and ethylene–octene copolymers. From 0 to 3% mole fraction of branch points, they found identical melting temperature–composition relations for the two copolymers studied. However, their results were several degrees higher than those for the copolymers in random sequence re-

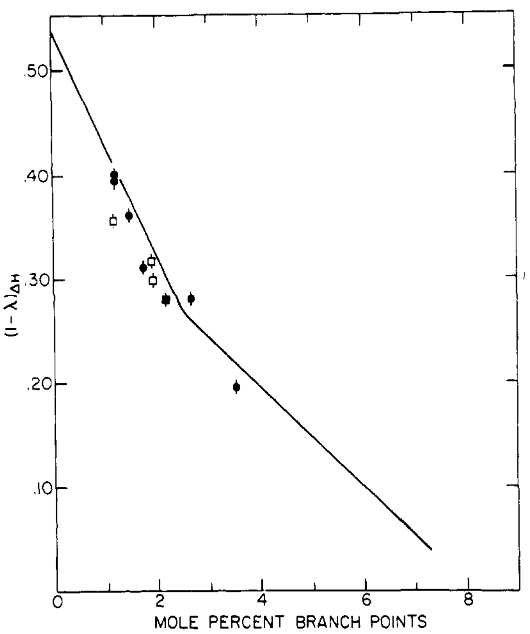

Figure 2. Plot of degree of crystallinity, calculated from enthalpy of fusion, against mole percent branch points. Copolymers with most probable molecular weight distribution: (ф) ethylene–butene; (♦) ethylene–hexene; (▮) ethylene–octene. Solid curve reproduced from ref 1.

ported here. We thus have another example of the fundamental principle that the melting temperature of a copolymer does not depend on composition per se but on the details of the sequence distribution of the counits.

Degree of Crystallinity. It is of interest to examine the level of crystallinity that is attained in relation to the pertinent structural factors and to compare the results that are obtained by the different methods. For a given counit content, there is a limited molecular weight range in the data of Table I. Within this limitation, we find a small but significant decrease in the degree of crystallinity with increasing molecular weight at a fixed branching content. It had been thought that for fractions of high-pressure branched polyethylene and hydrogenated polybutadienes the level of crystallinity was essentially independent of molecular weight except in the extreme limits of chain length.[16] This conclusion was based on data covering a relatively restricted molecular weight range. The results found here indicate that this conclusion was not correct. A more detailed study to be reported shortly,[20] which covers a very wide range in molecular weights of hydrogenated polybutadienes, indicates that there is a significant effect of chain length on the level of crystallinity that is attained, in agreement with the implications of the present results. Therefore, for the comparison study, which is the main interest in the present context, we limit ourselves to the study of the same copolymers as given in Figure 1.

We have determined the degree of crystallinity by three different methods by measuring the enthalpy of fusion, the density, and the Raman internal modes. We have previously found, with copolymers of molecular weight about 80 000, that the degree of crystallinity decreases very rapidly with increasing side group content but is independent of the chemical nature of the side group.[1] Figure 2 is a plot of the degree of crystallinity calculated from the enthalpy of fusion for the copolymers having a most probable molecular weight distribution. The solid curve that is drawn in this figure is a reproduction of the previous data. Very good agreement is obtained between the two studies, and we confirm that the degree of crystallinity is independent of the side group.

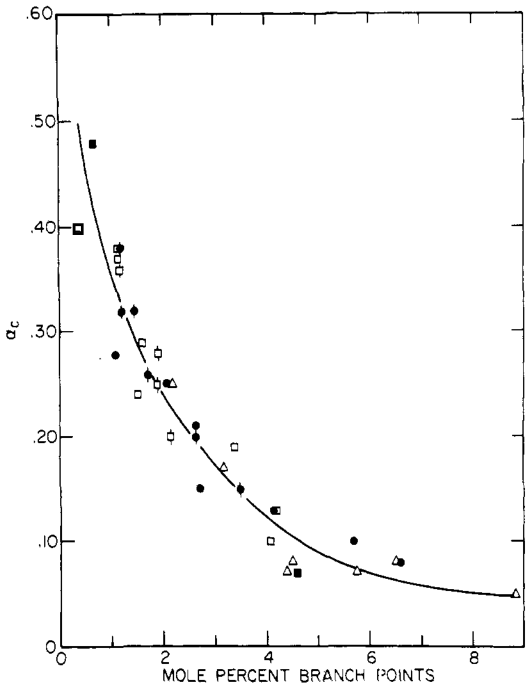

Figure 3. Plot of degree of crystallinity calculated from Raman internal modes, α_c, against mole percent branch points. From ref 1: (△) hydrogenated polybutadiene; (●) ethylene–vinyl acetate; (□) ethylene–butene; (■) ethylene–octene. From this work: (ф) ethylene–butene; (♦) ethylene–hexene; (▮) ethylene–octene.

In Figure 3, a comprehensive set of data for the level of crystallinity calculated from an analysis of the Raman internal modes, α_c, is given. These data included the same compositional fractions previously studied as well as the new copolymers. It is evident that the introduction of the noncrystallizing counits into the chain leads to a very rapid and continuing decrease in crystallinity with increasing side group content. Levels of crystallinity vary from about 0.48% for 0.5 mol % branches in ethylene copolymers to about 7% for 6 mol % branches. The chemical nature of the branches has virtually no influence on the crystallinity values for a given counit content. The values for $(1-\lambda)_{\Delta H}$ and α_c are very close to one another, as is indicated in Table I, and thus follow the pattern previously established for a variety of other polyethylene systems.[4,12,14,24,25]

The fact that the degree of crystallinity, irrespective of the method of determination, is independent of the chemical nature of the side group when the crystalline phase remains pure is to be expected for random-type copolymers.[21,22] (An obvious exception to this principle is for directly bonded CH_3 or Cl groups which enter the crystal lattice as an equilibrium requirement.[2-4,26,27]) The rapid decrease in crystallinity level with counit content is also a natural consequence of the structure of random copolymers. The length and number of sequences that are available to participate in the crystallization process is progressively reduced with increasing counit content.[22] On an equilibrium basis, all eligible sequences would participate in the crystallization process and the level of crystallinity can be calculated. However, since the equilibrium conditions are rarely if ever established during the crystallization of random copolymers, even under the most idealized conditions, the level of crystallinity that will be observed is substantially reduced below that expected.[28] The level of crystallinity measures the sum of all the crystalline sequences which are distributed among crystallites of different sizes. For the rapidly crystallized copolymers, the most probable crystallite thickness varies from 90 Å for 0.5 mol % branches to 45 Å for 4.5 mol %

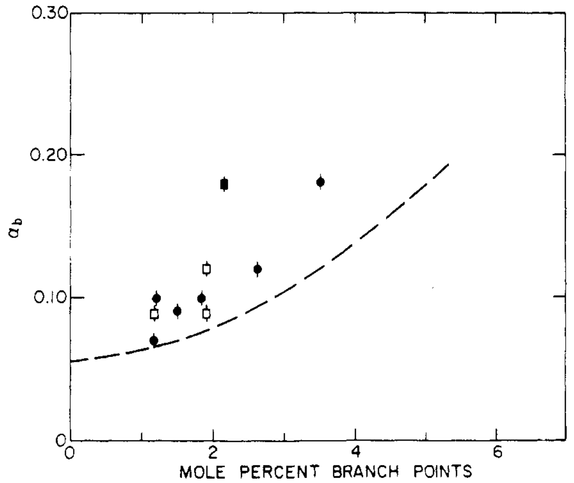

Figure 4. Plot of the fractions of the interfacial region, α_b, against the mole fraction of branch points. (□) Ethylene–butene; (◆) ethylene–hexene; (▮) ethylene–octene. Dashed curve reproduced from ref 1.

branches.[1] The level of crystallinity that is attained in an actual crystallization process is not a measure of the minimum sequence size that participates in the crystallization but rather is the sum over all possibilities.[29,30]

Interfacial Content. The degree of crystallinity determined from the density measurements depends on counit content in a very similar manner as was found from the enthalpy of fusion and the internal mode analysis. However, as indicated by the data in Table I, $(1 - \lambda)_d$ is always about 10% larger than the value determined from the heat of fusion. Small but significant differences in the level of crystallinity values obtained by these two methods have also been observed for a large number of linear, branched, and other ethylene copolymers.[12,14,24,25] These differences can be attributed, in a very consistent manner, to the contribution from the interfacial region.[12,14,24] Density measurements include a contribution from the interfacial region that is not reflected in the enthalpy of fusion measurements.

The interfacial content, α_b, can be determined from an analysis of the intenal mode region of the Raman spectrum. The values for α_b for the samples studied here are plotted in Figure 4 as a function of the branching content. The dashed line in the figure was taken from ref 1 and was drawn to demonstrate the general trend of interfacial contents with branching content. Copolymers with most probable molecular weight distributions have interfacial contents which are consistent with previous studies. The ethylene–1-octene copolymer studied, which has 2.14 mol % hexyl branch points, appears to have a larger interfacial content than the other copolymers at a comparable composition. However, although this is an intriguing result because of the size of the side group, we should not make generalizations based on only one data point. In terms of elucidating the detailed nature of the interfacial structure, this is a point worth pursuing with additional compositions of this copolymer.

For a large number of polyethylene-type polymer, it has been found that when the sum of the core crystallinity and interfacial content, $\alpha_c + \alpha_b$, is plotted against $(1 - \lambda)_d$ a 45° straight line results. A very similar result is found with the present data. There is then a quantitative self-consistency in interpreting the difference between $(1 - \lambda)_d$ and $(1 - \lambda)_{\Delta H}$ as representing the interfacial content.

An interesting set of data that results from these studies is illustrated in Figure 5 where α_b is plotted against M_w for the ethylene–1-hexene copolymers whose branch point contents are in the range 1.2–1.7 mol %. There is clearly an invariance in α_b with molecular weight. This result for copolymers is quite different from that found for homopolymers where interfacial content increases with molecular weight[12,25] Although there is invariance in α_b with molecular weight, there is a continuous decrease in the core crystallinity with increasing chain length. Changes in phase structure can thus be controlled and should have applicability in the study of other macroscopic properties of crystalline polymers.

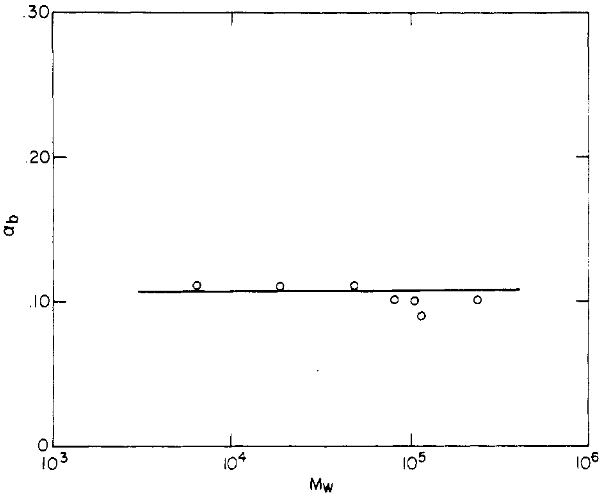

Figure 5. Plot of the fraction of the interfacial region, α_b, against the molecular weight for ethylene–hexene copolymers.

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Registry No. (Ethylene)(butene) (copolymer), 25087-34-7; (ethylene)(hexene) (copolymer), 25213-02-9; (ethylene)(octene) (copolymer), 26221-73-8.

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Mechano Ions Produced by Mechanical Fracture of Solid Polymer. 5. Cationic Polymerization of Isobutyl Vinyl Ether Initiated by the Mechano Cation of Poly(vinylidene fluoride)

Masato Sakaguchi

Ichimura Gakuen Junior College, Uchikubo 61, Inuyama 484, Japan

Hiromu Kinpara, Yasurō Hori, Shigetaka Shimada, and Hisatsugu Kashiwabara*

Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya 466, Japan.

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ABSTRACT: Poly(vinylidene fluoride) (PVDF) was fractured with isobutyl vinyl ether (IBVE) by using a vibration glass ball mill in vacuum in the dark at 77 K. Poly(vinyl isobutyl ether) (PVIBE) homopolymer ($\bar{M}_w = 6.2 \times 10^4$, $\bar{M}_n = 2.3 \times 10^4$) was obtained in the mixture. This result suggests that mechano cations were produced by heterolytic bond scission of carbon–carbon bonds in the PVDF main chain, and a cationic polymerization of IBVE was initiated by the mechano cations. A mechanism of the cationic polymerization of IBVE is proposed.

Introduction

It has been established that mechano radicals are produced by mechanical fracture of polymers at low temperature.[1-16] The radicals, chain-end-type free radicals, are produced by "homolytic bond scission" of carbon–carbon bonds in the polymer main chain. One of the authors (M. S.) has previously reported that radical polymerizations of methyl methacrylate and ethylene were initiated by the mechano radicals in vacuum at 77 K.[17,18]

Recently, we have reported that anions in various fractured polymers are detected by ESR spectroscopy using an electron-trapping technique.[19-22] It was proposed in these reports that "mechano anions" are produced by "heterolytic bond scission" of carbon–carbon bonds in the polymer main chain, and the yield of the mechano anions seems to increase with the polarity of the carbon–carbon bond owing to a substituent group bonded to the carbon in the polymer main chain.[22]

Experimental Section

PVDF (Kynar 720) was dissolved in boiling methyl ethyl ketone with 33% (volume) acetone, cooled, filtered, dried in vacuum at room temperature for 3 days, and further dried in vacuum at 323 K for 9 h. IBVE (Tokyo Kasei Co Ltd.) was washed with a 10% aqueous solution of sodium hydroxide, separated from the aqueous solution, boiled on sodium metal for 1 h, and distilled. The IBVE was degassed by freeze–pump–thaw on sodium metal, distilled 2 times at 243 K, and contacted with PVDF under vacuum. Mechanical fractures of PVDF with or without IBVE were carried out by using a vibration glass ball mill under vacuum in the dark at 77 K for 21 h.[8] After milling, the whole ESR sample tube connected to the glass ball mill was placed in liquid nitrogen, and the powdered sample was dropped into the ESR sample tube within 1 s. ESR spectra were obtained at a microwave power level of 0.04 mW and 100-kHz field modulation in the dark at 77 K by a JEOL JES-FE3XG ESR spectrometer (X-band) coupled to a Melcom 70 minicomputer (Mitsubishi Electric Co.).

1,1-Diphenyl-2-picrylhydrazyl (DPPH) was used to calibrate the magnetic field position on the ESR spectra.

In order to eliminate IBVE monomers, the fractured PVDF with IBVE was air-dried for 4 days and further dried under vacuum at room temperature for 31 h. This sample is referred to as "dried sample" in this article. A part of the dried sample was washed with toluene for 7 h by using a Soxhlet extractor. A residue of the extraction was dried in vacuum at room temperature for 31 h. This residue will be referred to as "residue sample". The extract obtained by the Soxhlet extractor was precipitated with methanol, air-dried for 3 days, and further dried under vacuum at room temperature for 2 days. This sample will be called the "extracted sample". A film of the extracted sample for observation of FT-IR spectra was obtained from a KBr disc from benzene solution. In order to eliminate benzene, the film on the KBr disc was dried under vacuum at room temperature for 68 h.

FT-IR absorbance spectra with 50 times accumulation were obtained by a JEOL JIR-100 FT-IR spectrometer using a KBr method at the FT-IR division of the Instrument Center of Nagoya Institute of Technology. The molecular weight of the extracted sample was obtained by gel permeation chromatography using a TOYO SODA HLC-803D GPC.

Results and Discussion

The ESR spectrum (Figure 1) of fractured PVDF without IBVE was observed at a high microwave power level of 0.4 mW with high amplification. Small humps (indicated with arrows) on both sides of the spectrum having a strong broad singlet in the center are called wing peaks. Figure 1 shows wing peaks with a hyperfine splitting constant of 43.0 mT and an inner triplet with about 2.4 mT superposed on the broad singlet in the center of the spectrum. The wing peaks, due to $2A_\parallel$ from two α-F atoms, indicate that homolytic bond scission of the PVDF main chain occurs, which produces a pair of mechano radicals (chain-end-type free radicals): $-CF_2^\bullet$ (I)[8,22] and $^\bullet CH_2-$ (II). Accordingly, the inner triplet is assigned to the mechano radical of $^\bullet CH_2-$.

The ESR spectrum (Figure 2) from the fractured PVDF with IBVE was found to have a large increase of radical concentration even at a power level of 0.04 mW and with lower amplification. Figure 2 shows wing peaks (marked with arrows, observed at 0.4 mW with high amplification) with a hyperfine splitting constant of 43.0 mT and a inner triplet (1:2:1) spectrum with a splitting of 2.2 mT superposed on an unknown broad singlet in the center of the

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